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(19) **United States**(12) **Patent Application Publication** (10) **Pub. No.: US 2003/0135939 A1**  
Sun et al. (43) **Pub. Date: Jul. 24, 2003**(54) **POLYVINYLAMINE TREATMENTS TO  
IMPROVE DYEING OF CELLULOSIC  
MATERIALS****Publication Classification**(51) **Int. Cl.<sup>7</sup>** ..... **D06M 13/322**  
(52) **U.S. Cl.** ..... **8/518; 8/536**(76) **Inventors: Tong Sun, Neenah, WI (US); Jeff  
Lindsay, Appleton, WI (US)**(57) **ABSTRACT**

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Textile materials, including paper webs, treated with a polyvinylamine polymer and a second agent that interacts with the polyvinylamine polymer is disclosed. The second agent added with the polyvinylamine polymer can be, for instance, a polymeric anionic reactive compound or a polymeric aldehyde-functional compound. When incorporated into a paper web, the combination of the polyvinylamine polymer and the second agent provide improved strength properties, such as wet strength properties. In an alternative embodiment, the polyvinylamine polymer and the second polymer can be applied to a textile material for increasing the affinity of the textile material for acid dyes.

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disintegration in the British disintegrator as specified above. The slurry was then diluted with deionized water to a volume of 8 liters. A first chemical (if used) was then added to the low consistency slurry as a dilute (1.0%) solution. The slurry was mixed with a standard mechanical mixer at moderate shear for 10 minutes after addition of the first chemical. A second chemical (if used) was then added and mixing continued for an additional 2-5 minutes. All stages experienced a substantially constant agitation level. Handsheets were made with a target basis weight of about 60 gsm, unless otherwise specified. During handsheet formation, the appropriate amount of fiber slurry (0.625% consistency) required to make a 60 gsm sheet was measure into a graduated cylinder. The slurry was then poured from the graduated cylinder into an 8.5-inch by 8.5-inch Valley handsheet mold (Valley Laboratory Equipment, Voith, Inc.) that had been pre-filled to the appropriate level with water. Web formation and drying is done as described in the default handsheet method described above, with the exception that the wet web in the Valley hydraulic press was pressed for one minute at 100 psi instead of 75 psi.

#### Tensile Tests

**[0148]** Handsheet testing is done under laboratory conditions of  $23.0 \pm 1.0^\circ \text{C}$ .,  $50.0 \pm 2.0\%$  relative humidity, after the sheet has equilibrated to the testing conditions for four hours. The testing is done on a tensile testing machine maintaining a constant rate of elongation, and the width of each specimen tested is 1 inch. The specimen are cut into strips having a  $1 \pm 0.04$  inch width using a precision cutter. The "jaw span" or the distance between the jaws, sometimes referred to as gauge length, is 5.0 inches. The crosshead speed is 0.5 inches per minute (12.5 mm/min.) A load cell is chosen so that peak load results generally fall between about 20 and about 80 percent of the full scale load (e.g., a 100N load cell). Suitable tensile testing machines include those such as the Sintech QAD IMAP integrated testing system or an MTS Alliance RT/1 universal test machine with TestWorks 4 software. This data system records at least 20 load and elongation points per second.

#### Wet Tensile Strength

**[0149]** For wet tensile measurement, distilled water is poured into a container to a depth of approximately  $\frac{3}{4}$  of an inch. An open loop is formed by holding each end of a test specimen and carefully lowering the specimen until the lowermost curve of the loop touches the surface of the water without allowing the inner side of the loop to come together. The lowermost point of the curve on the handsheet is contacted with the surface of the distilled water in such a way that the wetted area on the inside of the loop extends at least 1 inch and not more than 1.5 inches lengthwise on the specimen and is uniform across the width of the specimen. Care is taken to not wet each specimen more than once or allow the opposite sides of the loop to touch each other or the sides of the container. Excess water is removed from the test specimen by lightly touching the wetted area to a blotter. Each specimen is blotted only once. Each specimen is then immediately inserted into the tensile tester so that the jaws are clamped to the dry area of the test specimen with the wet area approximately midway between the span. The test specimen are tested under the same instrument conditions and using same calculations as for Dry Tensile Strength measurements.

#### Soluble Charge Testing

**[0150]** Soluble charge testing is done with an ECA 2100 Electrokinetic Charge Analyzer from ChemTrac (Norcross, Ga.). Titration is done with a Mettler DL21 Titratrator using 0.001N DADMAC (diallyl dimethyl ammonium chloride) when the sample is anionic, or 0.001N PVSK (potassium polyvinyl sulphate) when the sample is cationic. 500 ml of the pulp slurry prepared for use in handsheet making (slurry having about 1.5 g of fibers) is dewatered on a Whatman No. 4 filter on a Buechner funnel. Approximately 150 ml of filtrate (the exact weight to 0.01 grams is recorded for soluble charge calculations) is withdrawn and used to complete the titration. The streaming potential (streaming current) of the filtrate is then measured after 5 to 10 minutes, once the reading has stabilized. The sign of the streaming potential is then used to determine which reagent to apply in titration. The titration is complete when the current reaches zero. Soluble charge is calculated using the titrant normality (0.001N), titrant volume consumed, and filtrate weight; soluble charge is reported in units of milliequivalents per liter (meq/L).

#### Example 1

**[0151]** The strength benefits of polyvinylamine were explored with application to an uncreped through-dried tissue having a basis weight of 43 gsm, generally made according to the uncreped through-air dried method as disclosed in U.S. Pat. No. 5,048,589 to Cook et al. The tissue was made from a 50/50 blend of Fox River RF recycled fibers and Kimberly-Clark Mobile wet lap bleached kraft softwood fibers (Mobile, Ala.). The fibers were converted to a dilute slurry of about 0.5% consistency and formed into a web onto a pilot paper machine operating at 40 feet per minute. The embryonic web was dewatered by foils and vacuum boxes to about 18% consistency, whereupon the web was transferred to a through drying fabric with 15% rush transfer, meaning that the through drying fabric traveled at a velocity 15% less than the forming wire and that the differential velocity transfer occurred over a vacuum pickup shoe, as described in U.S. Pat. No. 5,667,636 to Engel et al. Through drying was done on a 44 GST through-drying fabric from AstenJohnson Company (Charleston, S.C.). No wet strength agents were added, resulting in a sheet with minimal wet strength. The tissue was cut to either 5-inch by 8-inch rectangles each having a weight of about 1.2 grams (room conditions of 30% RH and  $73^\circ \text{F}$ .) or to 8-inch by 8-inch rectangles with a dry mass of about 1.85 grams.

**[0152]** The cut tissues were treated in six different trials, labeled A through F and described below. In these trials, the polymeric anionic reactive compound used was BEL-CLENE® DP80 (Durable Press 80), a terpolymer of maleic anhydride, vinyl acetate, and ethyl acetate from FMC Corporation. This was prepared as a 1% by weight aqueous solution in deionized water. The PARC solution also included sodium hypophosphite (SHP) as a catalyst, with one part of SHP for each two parts by weight of polymeric reactive compound (i.e., 0.5% SHP).

**[0153]** The polyvinylamine compound used was either Catiofast® PR 8106 or Catiofast® PR 8104, both by BASF (Ludwigshafen, Germany), each diluted with deionized water to form an 0.5 wt % solution. These compounds include forms of polyvinylformamide which have been

hydrolyzed to various extents to convert the formamide groups to amine groups on a polyvinyl backbone. CatioFast® 8106 is about 90% hydrolyzed and Catiofast 8104 is about 10% hydrolyzed.

[0154] In the following trials, application of solutions to the web was done by spraying both sides of the web with a spray of the solution generated by a hand-held spray bottle.

[0155] Trial A: 2.9 g of PARC solution were added to a 5-inch by 8-inch tissue web for a PARC add-on level of 2.5% on a dry solids basis (PARC solids mass/dry fiber mass\*100%). The moist web was dried and cured in a convection oven at 160° C. for 13 minutes. No polyvinylamine was added.

[0156] Trial B: 1.25 g of PARC solution were added to a 5-inch by 8-inch tissue web for a PARC add-on level of 1.1% on a dry solids basis. The moist web was then sprayed with 2.7 g of Catiofast® 8106 solution for a polyvinylamine add-on of 1.2% on a dry solids basis (polyvinylamine solids mass/dry fiber mass\*100%). The moist web was dried and cured in a convection oven at 160° C. for 18 minutes.

[0157] Trial C: 2.85 g of Catiofast® 8106 solution were added to a 5-inch by 8-inch tissue web for a polyvinylamine add-on level of 2.5% on a dry solids basis. The moist web was then sprayed with 0.6 g of PARC solution for a PARC add-on of 0.26% on a dry solids basis (polyvinylamine solids mass/dry fiber mass\*100%). The moist web was dried and cured in a convection oven at 160° C. for 16 minutes.

[0158] Trial D: 4.54 g of Catiofast® 8106 solution were added to a 5-inch by 8-inch tissue web for a polyvinylamine add-on level of 4.0% on a dry solids basis. No PARC solution was added. The moist web was dried and cured in a convection oven at 160° C. for about 20 minutes.

[0159] Trial E: 3.78 g of Catiofast® 8104 solution were added to a 5-inch by 8-inch tissue web for a polyvinylamine add-on level of 3.3% on a dry solids basis. No PARC solution was added. The moist web was dried and cured in a convection oven at 160° C. for 20 minutes.

[0160] Trial F: 2.65 g of PARC solution were added to a 8-inch by 8-inch tissue web for a PARC add-on level of 1.5% on a dry solids basis. The moist web was then sprayed with 3.96 g of Catiofast® 8104 solution for a polyvinylamine add-on of 1.1% on a dry solids basis. The moist web was then dried and cured in a convection oven at 160° C. for about 20 minutes.

[0161] Samples were tested in a conditioned Tappi laboratory (50% RH, 73° F.) for CD wet tensile strength using an MTS Alliance RT/1 universal testing machine running with TestWorks® 4 software, version 4.04 c. Testing was done with 3-inch wide sample strips cut in the cross-direction, mounted between pneumatically loaded rubber-surfaced grips with a 3-inch gauge length (span between upper and lower grips) and a crosshead speed of 10 inches per minute. For wet tensile testing, the sample strips were bent into a U-shape to allow the central portion of the strip to be immerse in deionized water. The sample with the central wet region was then mounted in the grips such that the grips did not contact wet portions of the tissue, whereupon the tensile test commenced. Delay time from immersion of the central portion of the sample to initiation of crosshead motion was about 6 seconds. Results are shown in Table 1. (Two tests

were conducted for Trial A, but the first test was with a gauge length of 2 inches instead of 3 inches as used for all other trials. Though not reported in Table 1, the resulting value for CD wet tensile was 1330 g/3 in with a stretch of 6.4%.) Results reported include the wet tensile strength, with units of grams per 3-inches sample width; percent stretch at peak load; and TEA or total energy absorbed with units of centimeters-grams of force per square centimeter.

TABLE 1

CD Wet Tensile Results for Example 1.			
Sample	Wet Tensile, g/3 in	Stretch, %	TEA
untreated tissue	102	NA	1.085
Trial A	1329	4.98	6.78
Trial B	1069	3.82	4.15
Trial B	804	3.98	4.37
Trial C	737	5.08	4.48
Trial C	696	6.06	5.54
Trial D	921	7.31	7.39
Trial D	877	6.94	6.36
Trial E	171	4.27	1.58
Trial E	149	3.34	1.04
Trial F	663	4.15	3.31
Trial F	548	4.07	2.93

[0162] When wetted, the tissue from Trial C had a spotted appearance showing scattered regions that did not wet. It was hypothesized that an interaction of the two compounds, the PARC and the polyvinylamine, resulting in a sizing effect, though apparently the spray application was not sufficiently uniform to have a uniform sizing effect across the tissue. The results with a more uniform application of the two compounds are explored in Example 2 below.

#### Example 2

[0163] The untreated tissue and the solutions of Example 1 were employed again to explore the generation of hydrophobic properties associated with Trial C. In this example, however, the tissue was treated with a uniform application of both compounds simultaneously. The polyvinylamine solution was directly mixed with the PARC solution prior to application to the tissue. Thus, 5 ml of 0.5% Catiofast® PR 8106 were mixed at 73° F. with 5 ml of the PARC solution. The solution rapidly became cloudy, as if a colloidal suspension had formed. A similar mixture was also prepared using 5 ml of 0.5% Catiofast® PR 8104 which were mixed with 5 ml of the PARC solution. This second mixture remained clear. It is believed that the more highly hydrolyzed Catiofast® PR 8106 solution formed polyelectrolyte complexes with the anionic polymer that created a colloidal suspension.

[0164] The two mixtures were then applied to separate regions of another 8-inch by 8-inch tissue sample. The cloudy mixture of Catiofast® PR 8106 with PARC solution was applied dropwise to a portion of the sheet until 2.78 ml had been applied to a region about 7-cm in diameter. The clear mixture of Catiofast® PR 8104 with PARC solution was also applied dropwise to a remote portion of the tissue until 1 ml had been added. The tissue web with two distinct wetted areas was then placed in a convection oven at 160° C. for 5 minutes, where it was dried and cured. The dried tissue was then wetted by pouring tap water onto the web. The region that had been treated with the clear mixture of